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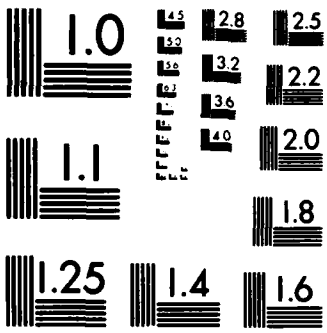

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A study has been made of the use of epitaxial crystallization of polymers, epitaxial polymerization and combinations of surface interactions and reactions to produce polymer epilayers with unique structures, morphologies, and properties. Classically, epitaxial crystallization of polymers is the oriented crystallization of polymers during interaction with a crystalline substrate. Epitaxial polymerization involves the crystallization of a monomer on a crystalline substrate and subsequent polymerization initiated

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20. ABSTRACT CONTINUED

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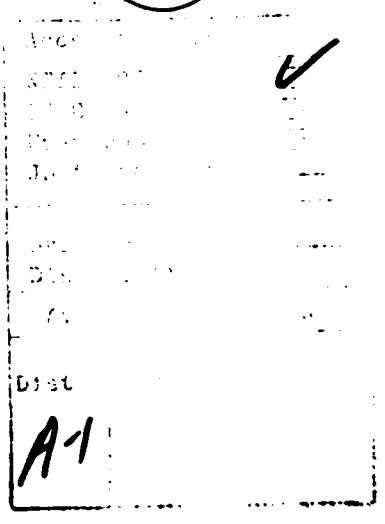

ARO 20280.1-CH

Final Report for
ARO Grant No. DAAG 29-83K-0130

Epitaxial Crystallization and Epitaxial Polymerization as Tools for Molecular Engineering

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July 30, 1986

1. Introduction and Objectives

Over the period of Grant DAAG 29-83K-0130 (start date 9/1/83), we have been exploring the use of epitaxial crystallization of polymers, epitaxial polymerization and combinations of surface interactions and reactions to produce polymer epilayers with unique structures, morphologies, and properties. Classically, epitaxial crystallization of polymers is the oriented crystallization of polymers during interaction with a crystalline substrate. Epitaxial polymerization involves the crystallization of a monomer on a crystalline substrate and subsequent polymerization initiated thermally, by ionizing radiation or by chemical doping. In addition, we have utilized a technique termed graphoepitaxy, which results from crystallization along deliberate deformities or topologies such as grooves in the substrate surface, and not necessarily crystallographic interactions.

The entire subject of epitaxial interactions and techniques has recently been reviewed in an article for the Encyclopedia of Polymer Science[1]. Since specific crystallographic or graphoepitactic interactions yield unique morphologies and in some cases new or unusual crystal structures[2], these processes should result in polymers with unusual structures and properties. One of our major interests is to produce polymers

that doped or undoped, may have useful electrical properties. Specifically, epitaxial polymerization allows one to "process" a monomer into coherent thin films, that may be ready for use after polymerization and doping. The following is a synopsis of the significant results obtained under Grant DAAG 29-83K-0130:

1. We have designed and built a film doping and conductivity measuring device that allows careful control of doping and accurate conductivity measurements.

2. We have been investigating the epitaxial polymerization of p-terphenyl on alkali halide crystals and on grooved poly(ethylene terephthalate) ("PET") film (i.e. graphoepitaxy). The terphenyl molecule has been deposited both from solution and the vapor phase. We have been able to control the direction of chain growth upon doping and polymerization of these thin films with AsF_5 . We have obtained a measure of anisotropy of conductivity in these oriented poly(p-phenylene) films of this molecular weight [1]. The resulting films are also quite stable for long periods of time in the atmosphere, after doping, and exhibit the highest known conductivity for poly(p-phenylene) thin films. We are in the process of working with perdeuterated terphenyl for NMR studies.

3. We have determined the first crystal structure for a

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1. L.W. Schacklette, and R.H. Baughman, private communication

poly(quinoline) through X-ray diffraction and calculation. The sample was prepared and supplied to us by John Stille of Colorado State University. In the process we have developed a more accurate method of calculating structures of aromatic polymers, with conducting properties. We wish to investigate the epitaxial crystallization with subsequent doping to high conductivity for this family of polymers.

4. We have produced large samples (10-100 grams) of highly pure and crystalline, partially fluorinated polyacetylene $-(CH{=}CF)_x-$ and intend to use epitaxial crystallization from the reacting solution to produce oriented samples. Dehydrofluorination of poly(vinylidene fluoride) by a phase transfer catalytic reaction produces this material. Also, we are attempting to produce oriented fibers of the substituted polyacetylene by heterogeneous reaction of poly(vinylidene fluoride) fibers as a template.

5. We are investigating the epitaxial crystallization of poly(phenylene sulfide) and intend to look at the anisotropy of conductivity in this polymer after doping. Initial epilayers have been successfully produced from high temperature solution crystallization.

6. We have developed new techniques for preparing high purity, highly stable polythiazyl $-(SN)_x-$ epitaxially in the normal crystalline form. We intend to investigate these

systems further to develop continuous processing methods for this unique, inorganic, conducting polymer.

2. Progress and Activities Associated with Work under ARO Grant DAAG 29-83K-0130

A. Publications

During the period of this grant, the following manuscripts have appeared:

1. "Epitaxial Growth of Conducting Polymers", L. Adams, G. Swei, J.B. Lando, and S.E. Rickert, Molecular Crystals and Liquid Crystals, 118, (1985).

2. "Epitaxial Processes", K.A. Mauritz, G.S. Swei, J.B. Lando and S.E. Rickert, in Mark Encyclopidia of Polymer Science and Engineering, 2nd Ed., Vol. 6, June 1986, Wiley, New York.

3. "The Variation of Polymer Morphology and Structure Through Surface Interactions", J.B. Lando, Physical Chemistry of Polymer Surfaces, K.L. Mittel Ed., Vol 1, pp. 559-567 (1983),Plenum, New York.

4. "Epitaxial Growth of Polydiacetylenes", S.E. Rickert, J.B. Lando, and S. Ching, ACS Symp. Ser., 233, 229(1983).

B. Submitted Papers

During the period of this grant, the following papers have been prepared for submission, or already submitted:

1. "Epitaxial Polymerization of p-Terphenyl", G. Swei, J.B. Lando, and S.E. Rickert.

2. "Electrical Properties of Ion Implanted p-Terphenyl", G. Swei, S.E. Rickert, and J.B. Lando.

3. "Preparation of Fluorinated Polyacetylene", B. Hahn, G. Swei, V. Percec, J.B. Lando, and S.E. Rickert.

4. "Structural Techniques in Aromatic Macromolecular Systems I. Nonbonded Potential Sets and Conjugation Energy", C.W. Burkhart and J.B. Lando.

5. "Structural Techniques in Aromatic Macromolecular Systems II. Analysis of Poly(2,2'-(p,p'-Biphenyl)-6,6'-bis(4-Phenylquinoline)), C.W. Burkhart, J.K. Stille, and J.B. Lando.

6. "Epitaxial Polymerization of the Cyclic Trime of Dichlorophosphazene", H. Nae, S. Ching, S.E. Rickert, and J.B. Lando.

7. "Epitaxial Crystallization of Poly(p-phenylene Sulfide)",

X. Qian, J.B. Lando, and S.E. Rickert.

C. Papers Presented

The following papers concerning work performed under this grant have been presented or are scheduled to be presented at national or international meetings"

1. L. Adams, J.B. Lando, and S.E. Rickert, "Novel Processing Methods in the Productions of Thin Films of Polythiazyl", American Physical Society, Baltimore, Maryland, March 1984.

2. G. Swei, S.E. Rickert, and J.B. Lando, "Epitaxial Polymerization of p-Terphenyl", American Physical Society, Baltimore, Maryland, March 1984.

3. S.E. Rickert, "New Processes for Thin Film Fabrication", American Chemical Society, New York, April 1986.

4. J.B. Lando, "Effect of Structure and Morphology on Electrical Properties of Conducting Polymers", Specialty Polymers '86, ElectroActive Polymers, Baltimore, Maryland, August 1986.

5. J.B. Lando, G. Swei, and S.E. Rickert, "Possible Methods of Processing Conducting Polymers", Second SPSS International Polymer Conference, Tokyo, Japan, August 1986.

D. Graduate Students

The following graduate students have completed their theses and dissertations under this grant:

1. L. Adams - "Novel Processing Methods for Polythiazyl", M.S. 1984.

The following graduate students are currently completing their theses and dissertations under this grant:

1. G. Swei - "Epitaxial Polymerization of p-Terphenyl", Ph.D. 1986.
2. C. Burkhart - "Structural Studies of Polyquinolines, etc.", Ph.D. 1986.
3. Xuijun Qian - "Epitaxial Crystallization of Poly(Phenylene Sulfide)", M.S. 1987.
4. Maged Botros - "Epitaxial Crystallization of Quinoline Polymers", Ph.D. 1989.

E. Inventions under Contract

1. A new process has been developed to produce polythiazyl $(SN)_x$ using a co-catalyst and monomer system. This process directly leads to high-purity polymer, with a higher degree of purity and crystallinity than normally produced. Thus,

this is the first process invented for the production of thin polythiazyl films and coatings, which can be easily scaled-up to a commercial process. Applications involving use of this coating on plastic films and fibers as an antistatic coating should be studied.

2. p-terphenyl has been successfully crystallized in the form of thin films and coatings, using alkali-halides and oriented cellulose acetate substrates, and the trimer has been polymerized in the solid-state by exposure to AsF_5. The invention stems from our novel ability to control the orientation of the resulting polymer, and therefore, the overall film conductivity, by detail control over polymer morphology and orientation. Again, this process can be easily scaled-up, and should be studied for possible use as antistatic coatings on plastic films and fibers.

3. Work Accomplished Under Grant No. DAAG 29-83K-0130

The following is a brief summary of some of the highlights of the work accomplished during the previous grant period:

1. Epitaxially crystallized p-terphenyl thin films have been reacted with a dilute (15%), high pressure (65 torr) AsF_5 / Ar mixture at room temperature for periods up to 14 hours. Final polymer films exhibiting chain directions normal to the substrate exhibited through film conductivities near 0.6 S/cm. The increase in conductivity is accompanied by a dramatic color change from clear to emerald green. Subsequent exposure to ammonia gas rapidly "clears" the film and conductivity rapidly drops as well (i.e. the film has been compensated).

2. Evidence for the polymerization of p-terphenyl to poly(p-phenylene) is given by FTIR studies of the annealed product of the terphenyl - AsF_5 reaction. Annealing the product to 370° C forces both unreacted p-terphenyl, and compensated dopant (e.g. NH_3 - AsF_5 complex) to sublime. The absorption bands at 800 and 765 cm^{-1} are due to C-H out of plane vibrations of the para and mono substituted rings and can be used to estimate the degree of polymerization.

3. The morphology of doped p-terphenyl has been examined by scanning electron microscopy, showing cracked, swollen, but still oriented epilayer films.

4. Uniform p-terphenyl thin films (e.g. thicknesses between 80 and 600 nm) were vapor deposited onto interdigitated electrodes, fabricated by photolithography, and patterned on a half micron thick gold film evaporated on a 2 inch silicon wafer. Subsequntly, these films were ion implanted with As, P, and Ar to dose levels near 10^{16} ions / cm^2. All three samples showed conductivities near 10 S/cm, but DRIFT studies indicated that the samples had extensively carbonized as well as polymerized.

5. Epilayers of poly(phenylene-sulfide) were successfully grown from a dilute 1-chloronaphthalene solution at 180-200 ^{o}C. The normal crystal phase was clearly observed in the rodlike, biaxially oriented crystals aligned diagonally, in the usual manner, on the NaCl surface. Films are being prepared for doping and conductivity studies.

6. A process has been developed for the reliable production of stable films of polythiazyl from either S_2N_2 or SN: monomers. This work is being expanded by development of a continuous process for coating films and fibers with epilayers of polythiazyl. It should be emphasized that this modification of the usual manner of $(SN)_x$ formation results in polymer that exhibits greater stability in moist

air than conventional materials.

7. Unaxially oriented crystalline fibers of poly(2,2' - (p,p'-biphenyl)-6,6-bis(4-phenylquinoline) ("PBPQ") supplied by John Stille of Colorado State University were subjected to structure analysis via molecular packing analysis and x-ray diffraction techniques. The packing analysis used Buckingham 6,1 potentials of Williams and Cox to predict possible unit cells. The quinoline and biphenyl moieties were modelfitted with crystal data. It should be noted that optimal potential functions for aromatic systems were developed for this work. Epitaxial crystallization of these quinoline polymers will be undertaken and conductivity as a function of doping and orientation will be investigated.

8. Poly(vinylidene fluoride) ("PVDF") has been dehydrohalogenated in solution and heterogeneously as fibers and film using NaOH and a phase transfer catalyst (tetra-n-butylammonium hydrogen sulphate). Complete dehydrohalogenation has been obtained yielding highly crystalline $-(CH{=}CF)_x-$, a fluorinated polyacetylene. A similar reaction using poly(trifluoro ethylene) yields $-(CF{=}CF)_x-$. Epitaxial experiments involving precipitation on suitable substrates from reacting solutions are underway.

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